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Microencapsulation of Pesticides by Interfacial Polymerization Utilizing Isocyanate or Aminoplast Chemistry†

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Abstract: Interfacial polymerization microcapsulation processes based on isocyanate or aminoplast chemistry, where all wall-forming reactants are placed in the dispersed oil phase are described. Emphasis is placed on mechanism of interfacial reactions, physical nature of the resulting membranes and methods used to vary membrane permeability.

Pesticide microcapsule formulations can be used to reduce mammalian toxicity and extend activity, to control evaporation, to reduce phytotoxicity, to protect pesticide from rapid environmental degradation, to reduce leaching and to reduce pesticide levels in the environment. Examples are provided to demonstrate how pesticide performance characteristics can be altered using this type of formulation. © 1998 Society of Chemical Industry

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Key words: microcapsule formulations; isocyanate/aminoplast wall-forming reagents

1 INTRODUCTION

This paper will focus on microencapsulation of pesticide oils using interfacial polymerization processes based on the condensation of isocyanate or aminoplast monomers or pre-polymers where all of the wall-forming reactants are placed in the dispersed oil phase. However, in order to understand why this type of process offers unique advantages for the microencapsulation of pesticides, it is necessary to discuss the variety of processes which could be utilized for this purpose.

1.1 Categories of microencapsulation processes

Microencapsulation processes can be divided into three major categories.[1] In the *physical methods* category, wall material and core particles are physically brought together and the wall flows around the core particle to form the microcapsule. In the *phase separation* category, microcapsules are formed by emulsifying or dispersing the core material in an immiscible continuous phase in which the wall material is dissolved and caused to separate physically from the continuous phase and

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† One of a collection of papers on various aspects of agrochemicals research contributed by staff and collaborators of Zeneca Agrochemicals UK and Zeneca Ag Products USA. The papers were collected and collated by Dr B. C. Baldwin and Dr D. Tapolczay.

‡ This paper is dedicated to the memory of Kuo-Shin Lee (1950–1996).

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deposit around the core particles. In the *interfacial reaction* category, microcapsules are formed by emulsifying or dispersing the core material in an immiscible continuous phase and then an interfacial polymerization reaction is caused to take place at the surface of the core particles.

1.2 Physical methods

Physical methods that use an orifice surrounded by an annulus to bring wall and core together fall into two categories—biliquid extrusion nozzles or biliquid multiorifice centrifugal devices.[2,3] After forming the microcapsule, the polymer wall is hardened by chemical reaction, evaporation of solvent or cooling. These processes have limited utility for the microencapsulation of pesticides because throughput is low and particle sizes less than 100 μm cannot easily be produced.

Physical methods, such as spray-drying, spray-chilling and fluidized-bed spray-coating bring wall and core together *via* an atomization process.[4–6] As with the orifice–annulus devices, the microcapsule polymer wall is hardened either by evaporation of solvent or by cooling. These processes are somewhat limited by the fact that under some conditions not all of the pesticide is encapsulated nor do all of the polymer particles contain pesticide cores.

1.3 Phase separation methods

In the phase separation category, a pesticide oil is emulsified into an aqueous phase containing dissolved polymer(s). The dissolved polymer(s) can be forced out of solution (phase separated) by a variety of techniques (change in pH, addition of a non-solvent, addition of salt) and deposited around the oil particles.[7,8]

In a variation of these phase-separation methods, a water-soluble monomer or pre-polymer can be used as the polymer-forming material. This material is added to the aqueous phase, where solubility relations are such that as the polymerization proceeds, a water-insoluble polymer precipitates and the polymer deposits on the oil droplets. Condensates of formaldehyde with urea or melamine are frequently used as water-soluble pre-polymers for this type of process.[9] These pre-polymers are caused to polymerize in the aqueous phase by the addition of an acidifying agent.

These phase-separation techniques are useful for the microencapsulation of pesticides but suffer from process-control and pesticide-loading limitations. It is difficult to achieve reproducible phase-separation conditions, and, in addition, it is difficult to ensure that the phase-separated polymer will preferentially wet the core droplets. Since the polymer phase separates from the continuous phase in these processes, and hence causes flow resistance between forming microcapsules, it is not possible to produce pesticide microcapsule formulations with pesticide loadings much greater than 240 g AI litre^{-1}.

1.4 Interfacial polymerization reaction methods

1.4.1 Interfacial addition

Interfacial addition polymerization processes using unsaturated monomers have limited utility for the microencapsulation of pesticides due to the presence of impurities in technical pesticides which interfere with the action of the free-radical-producing catalysts.

1.4.2 Interfacial condensation

Interfacial condensation microencapsulation processes are very suitable for the microencapsulation of pesticides because they are characterized by high pesticide loading (typically 480 g AI litre^{-1}) and uncomplicated processing steps. Interfacial condensation microencapsulation processes can be divided into two general types.

Type I. One reactive monomer is incorporated in the organic phase and a second reactive monomer in the water phase. Typically the organic-phase monomer is a polyfunctional isocyanate and the water-phase monomer is a polyfunctional amine.[10–12] Interfacial polymerization occurs rapidly at ambient temperatures.

Type II. In this type of process, the monomers or pre-polymers are incorporated only in the oil phase and they are polymerized interfacially by increasing temperature, in the case of polyfunctional isocyanate monomers, or by increasing temperature and providing a surface-active acid catalyst in the case of aminoplast pre-polymers. It is the Type II interfacial condensation microencapsulation process which is the subject of this paper. The Type II process produces a unique asymmetric membrane at the interface which distinguishes it from the Type I process.

2 EXPERIMENTAL METHODS

A general method for producing laboratory samples using the Type II interfacial condensation microencapsulation process will be outlined below. Details of specific ingredients and conditions can be found in the references cited, both for the polyfunctional isocyanate monomer case and for the aminoplast prepolymer case.[13,14]

The process starts by dissolving monomers or pre-polymers in the pesticide oil to be encapsulated (Fig. 1) to form the organic phase. If the pesticide is a solid it must be dissolved in a water-immiscible solvent before the monomers or pre-polymers are added. The aqueous phase is then prepared by addition of emulsifiers and protective colloids to water. In the aminoplast process a surface-active sulfonic acid catalyst is also added to the aqueous phase. The next step in the process is to add

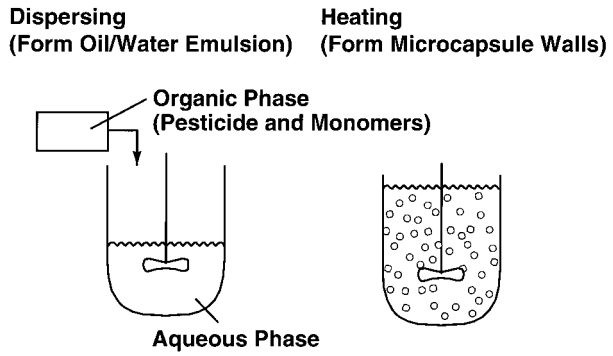


Fig. 1. Process steps in the Type II interfacial condensation microencapsulation process.

the organic phase to the aqueous phase with appropriate agitation to form an oil-in-water emulsion with an average particle size in the range 2–15 μm. Finally, microcapsule wall formation is initiated and completed by heating the batch to 50°C and holding at this temperature for 3 h. The microcapsule dispersion is then allowed to cool and the formulation is completed by the addition of buffering agents, a biocide and suspending agents.

3 RESULTS, DISCUSSION AND CONCLUSION

3.1 Type II interfacial condensation microencapsulation process based on polyfunctional isocyanate monomers or aminoplast pre-polymers

3.1.1 Mechanism of wall formation and resulting membrane morphology

In the case of the *polyfunctional isocyanate system* the monomers (Fig. 2) that are incorporated in the organic phase are polymethylene-polyphenylisocyanate (PMPPI) and toluene diisocyanate (TDI). PMPPI has an average isocyanate functionality of 3, although it may range from 2 to 8.

The wall-forming reaction (Fig. 3) is initiated by heating the oil-in-water emulsion to 50°C, at which point the isocyanate monomers are hydrolysed at the interface (slow step) to form amines which, in turn, react with unhydrolysed monomers at the interface to form the polyurea microcapsule wall (Fig. 4). This interfacial reaction occurs on the oil side of the interface and is limited to the interface because of the unavailability of water in the core of the oil particle. Water diffuses into the oil droplet at the interface and reacts with isocyanate monomers diffusing from the core of the particle to the interface. Because interfacial polymerization is initiated by water which is at the highest concentration right at the interface and at progressively lower concentrations as the distance increases from the interface, the resulting membrane is asymmetric in construction (Fig. 5). In Fig. 5 a scanning electron micrograph of an artificially broken microcapsule is shown (these pesticide capsules never break during application). Note the asymmetric nature of the membrane (thin outer dense layer supported by a much thicker spongy underlayer). The thin outer dense layer (about 0·05 μm or 500 Å in

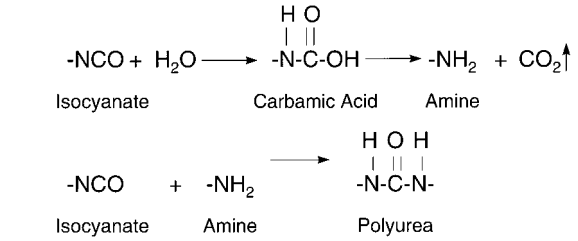


Fig. 3. Wall-forming reaction for the polyfunctional isocyanate microcapsule system.

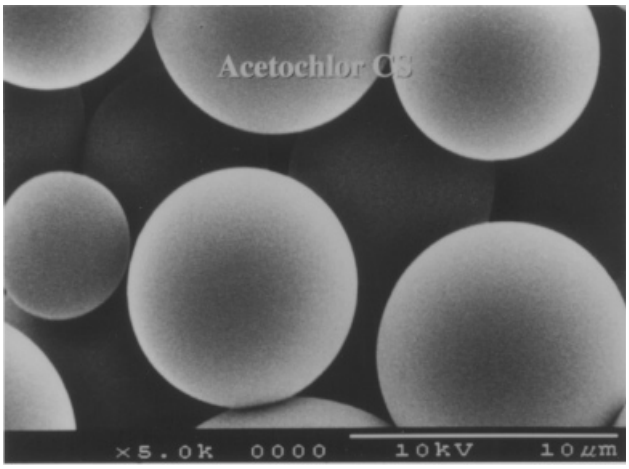


Fig. 4. Microcapsules made using the polyfunctional isocyanate microcapsule system—10 μm scale bar under photograph.

Fig. 5. Artificially broken microcapsule made using the polyfunctional isocyanate microcapsule system (note asymmetric membrane construction)—Magnification: 5200.

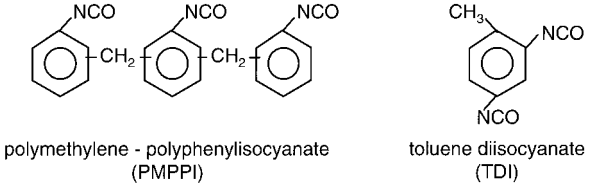


Fig. 2. Monomers used in the polyfunctional isocyanate microcapsule system.

thickness) is the working end of the membrane. It offers diffusional resistance to the flow of pesticide. The thicker spongy underlayer (about 0·5 μm) provides mechanical support. This unique asymmetric membrane construction is a direct result of the role of water in the interfacial polymerization reaction. The resulting asymmetric membrane looks very much like a reverse osmosis membrane. A transmitting electron microscope view (Fig. 6) of a microcapsule in cross-section (embedding resin used) also shows the asymmetric nature of the polyurea membrane. The thin dense outer-layer of the asymmetric membrane is very efficient in controlling the release of pesticides and hence these microcapsules have an unusually low microcapsule-wall to pesticide-core weight ratio. In addition, by varying a host of process parameters (see Section 3.1.2) this process is capable of producing microcapsules that have release rates that vary over orders of magnitude.

In the case of the *aminoplast pre-polymer system* the wall-forming agent (Fig. 7) that is incorporated in the organic phase is a butylated urea-formaldehyde pre-polymer with a molecular weight of approximately 1000. The urea-formaldehyde pre-polymer is butylated to impart oil solubility. The wall-forming reaction (Fig. 8) is initiated by adjusting the pH of the oil-in-water emulsion to 2·0 and then heating the emulsion to 50°C. At this point a butylated methylol group on the pre-polymer located on the oil side of the droplet interface is activated by the addition of a proton from the surface-active sulfonic acid catalyst, and this activated pre-polymer then reacts with a methylol group from another pre-polymer located on the oil side of the interface to form a methylene linkage (butanol and formaldehyde are also formed). Repetition of this interfacial reaction leads to the formation of an aminoplast microcapsule wall (Fig. 9). This interfacial reaction occurs on the oil side of the interface and is limited to the interface because the sulfonic acid catalyst is surface-active and

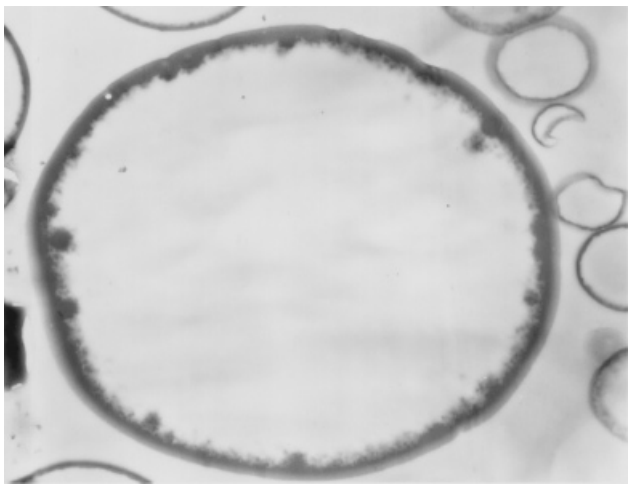


Fig. 6. A transmitting electron microscope view of a polyurea microcapsule in cross-section (embedding resin used)—Magnification: 2570.

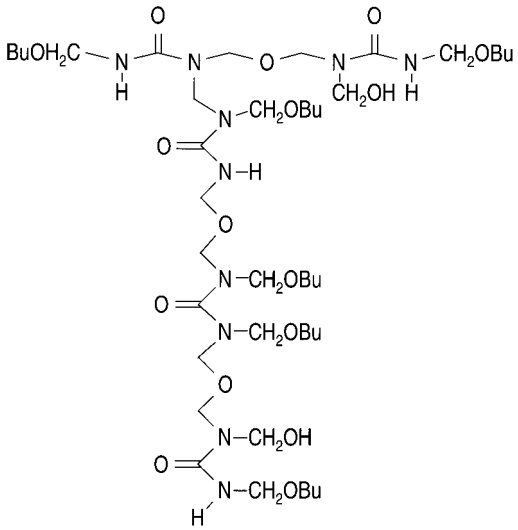


Fig. 7. Butylated urea-formaldehyde pre-polymer used in the aminoplast pre-polymer microcapsule system.

therefore transfers its proton to activate the butylated methylol group on the pre-polymer only at this location. The membrane produced in this microencapsulation process is also asymmetric (Fig. 10) because the concentration of acid-activated pre-polymer decreases rapidly as the distance from the interface increases. As with the asymmetric polyurea membrane formed from

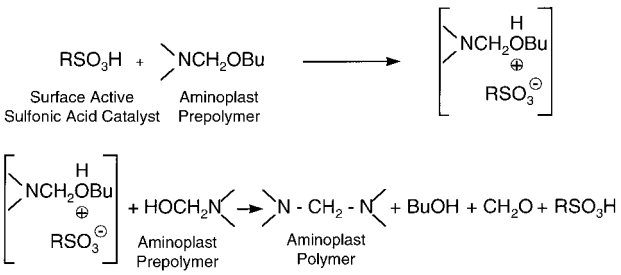


Fig. 8. Wall-forming reaction for the aminoplast pre-polymer microcapsule system.

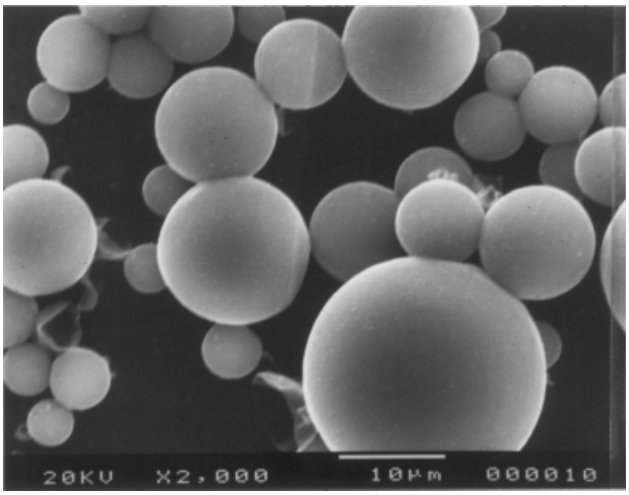


Fig. 9. Microcapsules made using the aminoplast pre-polymer microcapsule system—10 μm scale bar under photograph.

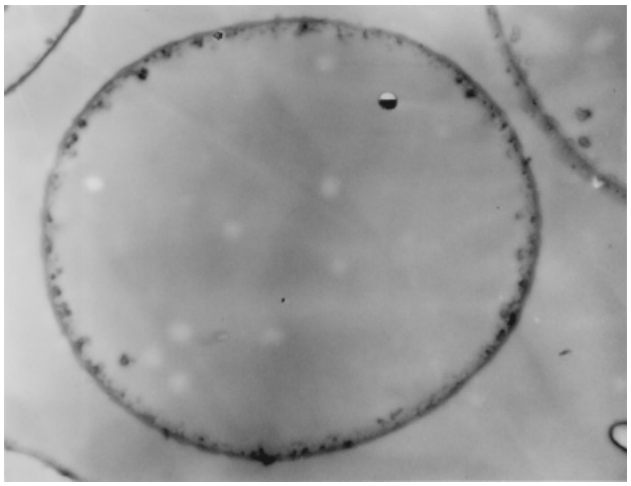
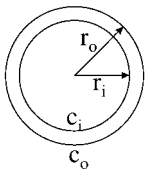


Fig. 10. A transmitting electron microscope view of an aminoplast microcapsule in cross-section (embedding resin used)—Magnification: 3425.



$$\frac{dM}{dt} = \text{Release Rate} = \frac{(4\pi r_o r_i)\, P\, (C_i - C_o)}{r_o - r_i}$$

$$P = KD$$

r = radius
P = Permeability
K = Solubility Coefficient
D = Diffusion Coefficient
C = Concentration

Fig. 11. Microcapsule release rate equation (diffusional mechanism).

isocyanates, this asymmetric aminoplast membrane is very efficient in controlling the release of pesticides and these aminoplast wall microcapsules have an unusually low microcapsule-wall to pesticide-core weight ratio. In addition, by varying a host of process parameters (see Section 3.1.2) this process is also capable of producing microcapsules that have release rates that vary over orders of magnitude.

The aminoplast interfacial reaction described above takes place at the oil/water interface at 50°C, whereas, in dry films, the acid-catalyzed reaction of butylated methylol urea-formaldehyde pre-polymers takes place at much higher temperatures (100–150°C).[15] This suggests that the protonated butylated methylol intermediate is stabilized at the water/oil interface by the presence of water and hence the activation energy for the reaction is lowered at the interface. As the distance from the interface increases the concentration of the water-stabilized protonated intermediate decreases and this also contributes to the formation of the localized asymmetric membrane.

3.1.2 Methods used to vary membrane permeability

The microcapsule release-rate equation (diffusional mechanism) is shown in Fig. 11. The release rate is directly proportional to surface area, permeability and concentration difference across the wall and is inversely proportional to wall thickness. The average particle radius (hence surface area) and wall thickness are generally fixed within narrow limits to satisfy process and physical stability considerations. The concentration difference across the wall is generally considered to be a constant when the microcapsule is exposed to a foliar or soil environment. The foliage or soil acts as a 'sink' for the pesticide and hence pesticide exists at a very low concentration at the outer surface of the microcapsule. Hence if the release rate from the microcapsule needs to be varied over orders of magnitude to accommodate the release of different pesticides with different modes of application, the most practical way of accomplishing this task is to vary the microcapsule wall permeability. The permeability is defined as the product of the diffusion coefficient and the solubility coefficient. For a given pesticide the diffusion coefficient can be varied by varying the cross-link density of the wall and the solubility coefficient can be varied by varying the chemical composition of the wall.

For the polyfunctional isocyanate system, the cross-link density can be varied by varying the ratio of trifunctional isocyanate (PMPPI) to toluene diisocyanate (TDI). The higher the ratio, the more cross-linking and hence the lower the diffusion coefficient and the lower the permeability. For the aminoplast pre-polymer system, the cross-link density can be increased by the addition to the organic phase of compounds which contain multiple hydroxy or mercapto groups capable of reacting with the methylol groups on the pre-polymer.

The solubility coefficient of the wall is related to the ease with which a given pesticide can partition from the core into the wall. The closer the chemical composition of pesticide is to the chemical composition of the wall, the greater the solubility coefficient and the greater the permeability. From a diagram (Fig. 12) which shows the polarity of the polyurea and aminoplast walls relative to each other and relative to Pesticide A and Pesticide B, it is clear that, for Pesticide A, the aminoplast wall would be a better barrier. However, the aminoplast wall would probably be too good a barrier for pesticide B because of their great dissimilarity in polarities.

3.1.3 Modification of performance characteristics of pesticides through microencapsulation

The Type II polyfunctional isocyanate microencapsulation system has been utilized commercially to modify the performance characteristics of herbicides (Table 1) and insecticides (Table 2). Examples of volatility

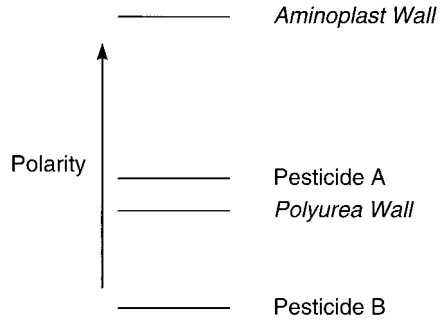


Fig. 12. Polarity of polyurea and aminoplast microcapsule walls relative to each other and relative to pesticide A and pesticide B.

reduction, phytotoxicity reduction, toxicity reduction and extension of pesticide activity are discussed below. For each of these examples, the release rate from the microcapsules needed to be optimized to reduce these side effects without loss in biological efficacy. These same general effects can be achieved through the use of other microencapsulation systems. However, the Type II polyfunctional isocyanate system allows for more precise optimisation because of the asymmetric nature of the membrane and the fact that the cross-link density, and hence release rate, can be varied incrementally over a wide range.

The thiocarbamate corn herbicide EPTC has a relatively high vapor pressure ($3{\cdot}4 \times 10^{-2}$ mm Hg at 25°C) and needs to be incorporated into the soil immediately on application in order to prevent high evaporative loss if an emulsifiable concentrate type formulation is used. Where immediate incorporation is not possible, the microencapsulated EPTC formulation allows incorporation to be delayed for up to 24 h without loss of biological activity.[16,17] Additionally, the microencapsulated EPTC formulation allows the applicator to reduce the rate of application of EPTC by approximately 15%.

The microcapsule formulation of the soil-applied sunflower herbicide flurochloridone can reduce phytotoxi-

TABLE 1
Commercial Microencapsulated Herbicides Produced Using Type II Polyfunctional Isocyanate System

Product trade name (concentration)[a]	*Active ingredient microencapsulated*	*Crop use*	*Benefit of microencapsulation*
Capsolane (36CS)	EPTC	Corn	Retarded volatilization and reduced rate of application
Racer ME (25CS)	Flurochloridone	Sunflower	Reduced phytotoxicity
TopNotch (38.4CS)	Acetochlor	Corn	Extended residual control
Fultime (28.8CS/19.2SC)	Acetochlor (inside microcapsule)/ Atrazine (outside microcapsule	Corn	Extended residual control

[a] (36CS) denotes 360 g liter^{-1} capsule suspension.

TABLE 2
Commercial Microencapsulated Insecticides Produced Using Type II Polyfunctional Isocyanate System

Product trade name (concentration)[a]	*Active ingredient microencapsulated*	*Crop use*	*Benefit of microencapsulation*
Dyfonate (43CS)	Fonofos	Winter wheat	Reduction of oral and dermal toxicity
Force Seed Treatment (30CS)	Tefluthrin	Winter wheat	Reduction of paraesthesia
Force Seed Treatment (20CS)	Tefluthrin	Sugar beets	Reduction of paraesthesia
Icon or Demand (10CS)	Lamda-cyhalothrin	Public health	Extension of activity reduction of paraesthesia
Karate (25CS)	Lamda-cyhalothrin	Cotton forestry horticulture	Reduction of paraesthesia

[a] (43CS) denotes a 430 g liter^{-1} capsule suspension.

city (compared to an emulsifiable concentrate formulation of the compound applied at the same rate) without loss of weed control.

The microcapsule formulation of the soil-applied corn herbicide acetochlor can be used to extend residual herbicide control. This is particularly important in no-till applications where growers apply herbicides as early as four weeks before planting.

Microencapsulation can be used effectively to reduce the toxicity of insecticides. Fonofos Seed Treatment (43 CS), recommended for the control of wheat bulb fly and wireworm in winter wheat, has the following acute toxicity.

Acute Oral LD_{50} (Rats)	2370 mg kg^{-1}
Acute Dermal LD_{50} (Rabbits)	1500 mg kg^{-1}

These values represent about a 100-fold reduction in oral toxicity and about a 10-fold reduction in dermal toxicity. In addition to reduced toxicity, other advantages of microencapsulated insecticide seed treatments over nonencapsulated insecticide seed treatments are:

- Reduced phytotoxicity
- Ability to coat seed with liquid insecticide without using absorbent carrier
- Controlled-release effect to extend activity

In the tefluthrin insecticide seed treatments (30CS and 20CS) for winter wheat and sugar beet, microencapsulation can be used to reduce paraesthesia (a sensation of prickling or tingling on the skin usually associated with irritation of sensory nerves). This effect is common to most pyrethroid insecticides and hence microencapsulation is also useful for reduction of paraesthesia with lambda-cyhalothrin (10CS and 25CS). In addition the lambda-cyhalothrin 10CS which is used in a variety of public health insect-control applications (in and around homes and food establishments) allows effective residual control to be extended to three months.

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REFERENCES

1. Scher, H. B., Microencapsulated pesticides. In *Controlled Release Pesticides*, ed. H. B. Scher. American Chemical Society, Washington DC, USA, 1977, pp. 126–44.
2. Somerville, G. R., British Patent 1142708, 1966.
3. Goodwin, J. T. & Somerville, G. R., Physical methods for preparing microcapsules. In *Microencapsulation Processes and Applications*, ed. J. E. Vandegaer. Plenum Press, NY, 1974, pp. 115–63.
4. Macaulay, N., Recording Paper Coated with Microscopic Capsules of Coloring Material, Capsules and Method of Making. US Patent 3016308, 1962.
5. Sparks, R. E. & Mason, N. S., Method for Coating Particles or Liquid Droplets. US Patent 4675140, 1987.
6. Hall, H. S. & Hinkes, T. M., Air suspension encapsulation of moisture sensitive particles using aqueous systems. In *Microencapsulation Processes and Applications*, ed. J. E. Vandegear. Plenum Press, NY, 1974, pp. 145–53.
7. Bakan, J. A., Microencapsulation using coacervation phase separation techniques. In *Controlled Release Technologies: Methods, Theory and Applications*, ed. A. F. Kydonieus. CRC Press, Boca Raton, FL, USA, 1980, pp. 83–105.
8. Scher, H. B. & Maars, G. J., Development and uses of microencapsulation. In *Controlled Delivery of Crop-Protection Agents*, ed. R. M. Wilkins. Taylor and Francis, London, 1990, pp. 65–90.
9. Matson, G. W., Microcapsule Containing Paper. US Patent 3516846, 1970.
10. Vandegaer, J. E., Encapsulation by Interfacial Polycondensation. US Patent 3577515, 1971.
11. Beestman, G. B. & Deming, J. M., Encapsulation by Interfacial Polycondensation, and Aqueous Herbicidal Composition Containing Microcapsules Produced Thereby. US Patent 4280833, 1981.
12. Beestman, G. B. & Deming, J. M., Encapsulation by Interfacial Polycondensation. US Patent 4417916, 1983.
13. Scher, H. B., Encapsulation Process and Capsules Produced Thereby. US Patent 4285720, 1981.
14. Scher, H. B. & Rodson, M., Microencapsulation Process. US Patent 4956,129, 1990.
15. Blank, W. J., Reaction mechanism of melamine resins. *J. Coating Technol.*, **51**(658) (1979).
16. Scher, H. B., Groenwold, B. E., Pereiro, F. & Purnell, T. J., Microencapsulated thiocarbamate herbicides. In *Proc. Brit. Crop Prot. Conf.—Weeds*, 1980, pp. 185–91.
17. Scher, H. B., Development of herbicide and insecticide microcapsule formulations. In *Proc. Internat. Symp. Control Rel. Bioact. Mater.*, 1985, pp. 110–11.